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ABSTRACT

Some epoxy plastic components (resins and curing agents) have been synthesized which contain fluorocarbons in their molecular structures. In some cases the fluorocarbon is part of the network structure upon which the strength of the plastic depends, and in all cases it is attached to the network by at least one covalent chemical bond. Among the properties that are obtained with selected resin systems are surface nonwetting by water, low internal absorption of water, and low surface friction of the cured plastics. In specific cases, low-melting or liquid res systems have been obtained which react upon the application of heat to yield plastics.

PROBLEM STATUS

AUTHORIZATION

FLUOROCARBON IN EPOXY PLASTICS

INTRODUCTION

The Navy has a substantial interest in the performance of organic polymers in the presence of water. These materials are being used in applications which require a high order of reliability, and in which the insidious effects of the environment present a major uncertainty regarding long-term performance. The use of organic adhesives to bond the wing structures of supersonic aircraft illustrates the point, for such structures are engineered to withstand the anticipated levels of dynamic loading with an adequate safety margin. However, after the aircraft has been soaked repeatedly in tropical rains, and the adhesive bonds have been weakened by water saturation, structural reliability based on the data obtained from fresh adhesives is unlikely to represent the actual condition.

Some future applications of epoxy adhesives in particular are critically dependent upon the abilities of these materials to resist the effects of water. A recent analysis of various prospective hull materials for deep-diving submarines showed that fiber-reinforced plastics are among the more promising candidates, provided that problems in fabrication and reliability can be overcome (1). The necessity for filament-winding plastics to have outstanding resistance to high-pressure water and dynamic fatigue over long time spans is obvious if such a demanding application is to be realized.

Among polymeric materials, those containing large percentages of fluorocarbon in the molecular structures are perhaps the least affected by water. Aliphatic fluorocarbons are exceptionally hydrophobic, and polytetrafluoroethylene is neither readily wetted on the surface by water, nor is much water absorbed internally. On the other hand, the class of polymers termed "epoxies" varies widely in response to water, depending upon the particular type of resin and curing agent employed. In general, the strongest epoxy plastics absorb the most water and are most likely to be damaged. Ultrastrong materials, such as the reaction product of 1,4-cyclohexane dioxide and metaphenylene diamine (2), may absorb as much as 10% water by weight and spall into flakes upon drying (Fig. 1). The common epoxies saturate with about 3% weight gain and dry without apparent damage (3). Adhesive bonds between such an epoxy and a substrate such as glass are probably more susceptible to damage than is the plastic itself.

In this work we have incorporated fluorocarbon segments into the complex molecular structures of cured epoxy resins. So far, the work has not involved basic fluorination studies, nor are the inclusions of fluorocarbons considered to be optimum from the standpoint of plastic strength and practical utility. Rather, the effort has been made to obtain epoxy components in which fluorocarbons in appreciable quantities are attached to the plastic network through at least one covalent chemical bond, as opposed to a physical inclusion or entrapment of fluorocarbon materials within the plastic. Some of the more promising systems are being evaluated in filament-wound structures subjected to dynamic fatigue in water. These and others have potential use as aircraft adhesives, fuel tank linings, self-lubricating plastic gears, barrier films, sonar dome and hydrofoil coatings or matrix resins, and in other applications for which a combination of the unique properties of epoxies with those of fluorocarbons would be advantageous.
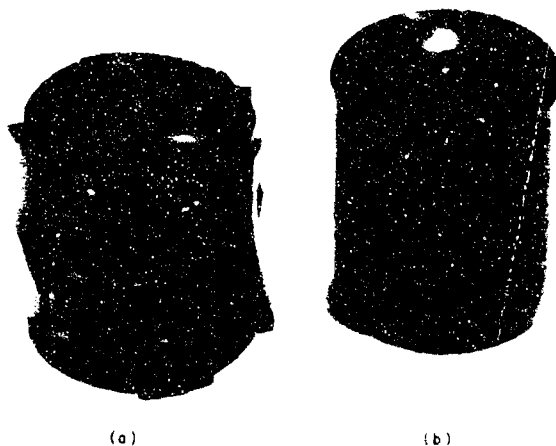
(a)   (b)

Fig. 1 – Effect of fluorine in the curing agent upon
the water resistance of a high-strength epoxy.
(a) Regular amine, and (b) fluorinated amine.

4,4'-DIGLYCIDYL ETHER OF OCTAFLUOROBIPHENYL

4,4'-dihydroxy octafluorobiphenyl was prepared from decafluorobiphenyl according
to a reported method (4). This material reacted like a typical diphenol (5) with an
excess of epichlorohydrin and alkali to form the diglycidyl ether

(I)
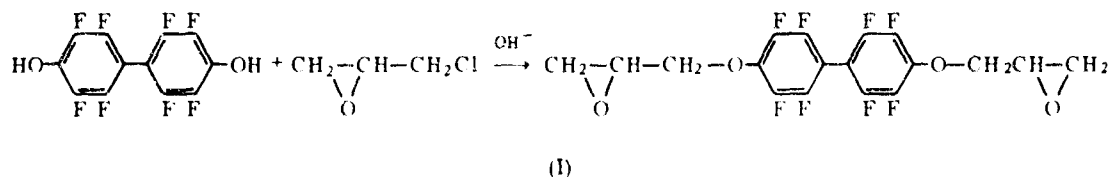
A solution containing 14.8 g (0.045 mole) of 4,4'-dihydroxy octafluorobiphenyl in
41.6 g (0.45 mole) of epichlorohydrin and 45 g of acetone was placed into a single-
necked, round-bottomed flask equipped with a magnetic stirrer and a reflux condenser.
Water (100 g) was added, and the flask contents were heated to the reflux temperature
on a silicone oil bath. An aqueous solution of sodium hydroxide (20% by weight) was
added in five equal increments, with a 15-min reaction time between increments. The
aqueous phase was then separated, and a sixth equal increment of sodium hydroxide
was added. The total quantity of alkali was 4.0 g (0.10 mole). After 15 min of addi-
tional reflux, 100 ml of water was added, the aqueous phase was separated and dis-
carded, and excess epichlorohydrin was removed at 160 C and 5-mm Hg pressure on
a rotary evaporator. The residue was a brown oily material weighing 17.8 g. It was
recrystallized twice from ethanol and once from methanol to yield 11.9 g (60% of
theoretical) of the diglycidyl ether of 4,4'-octafluorobiphenyl. Analytical samples were
prepared by recrystallizing the material four additional times from pure methanol.
The elemental analysis and physical properties are:

$$C_{18}H_{10}F_8O_4$$
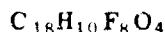
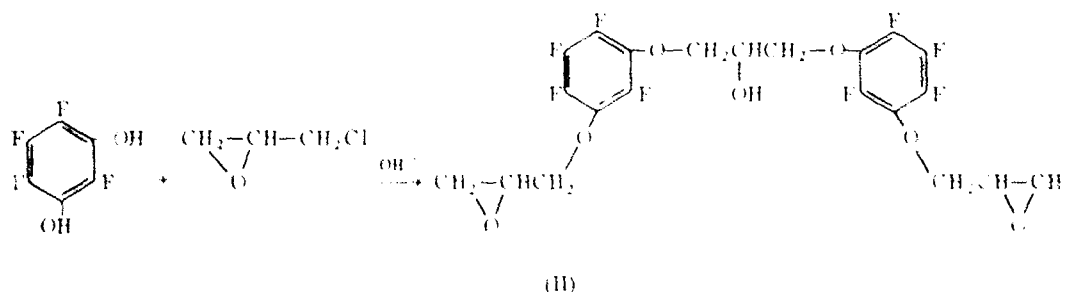|	Theory	Found
Carbon	48.88%	49.15%
Hydrogen	2.28%	2.50%
Fluorine	34.36%	34.43%
Epoxy equiv. wt.	221	242*

Melting point: 75-77°C

Major infrared bands: 1480, 1090, 990, 890, and 730 cm^{-1}.

The pure material is a white crystalline solid with a waxy appearance.

## GLYCIDYL ETHER OF TETRAFLUORORESORCINOL

A similar reaction with tetrafluororesorcinol (4) did not occur as uniquely or give as clear cut a product.

Tetrafluororesorcinol, 30.0 g (0.165 mole), epichlorohydrin, 213 g (2.31 mole), and water, 1.0 ml, were placed into a 500-ml, round-bottomed, single-necked flask fitted with a reflux condenser and a magnetic stirrer. An exothermic reaction began immediately. The flask was immersed in cold water until the temperature returned to ambient. Powdered sodium hydroxide, 16.0 g (0.40 mole), was slowly added through the condenser into the stirred reactants over a period of 2 hr. The flask contents were then heated to 110°C and stirred for an additional 2 hr. Excess epichlorohydrin was removed on a rotary evaporator, and a brown semisolid residue remained. This residue was extracted three times with 100-ml portions of hot benzene, and a solid polymeric residue with a chocolate-brown color remained in the flask. The benzene extracts were combined, and the solvent was evaporated on a warm water bath. More residual solvent was then stripped on a rotary evaporator. The brown liquid residue was then passed through a molecular still at 100°C and 250-μ Hg pressure to remove the last traces of epichlorohydrin. The residue was then passed through the molecular still again at 180°C and 200-μ Hg pressure to yield a clear distillate weighing 17.0 g (34.8% of theory for the diglycidyl ether of tetrafluororesorcinol). A 5.0-g portion of this material was then redistilled slowly at 175°C and 1-mm Hg pressure to obtain an analytical sample. The analytical results indicate that the material is principally the dimer

(II)

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*Found by pyridine hydrochloride titration.

having the following properties

$$C_{21}H_{16}F_8O_7$$
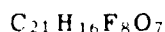
	Theory	Found
Carbon	47.37%	48.05%
Hydrogen	3.03%	5.02%
Fluorine	28.55%	22.69%
Epoxy equiv. wt.	266	250

Major infrared bands: 1500, 1030, and 900 cm[1].

FLUORINATED AROMATIC DIAMINES

Three aromatic diamines have recently become available commercially which are fluorinated on the aromatic rings: tetrafluoro-meta-phenylenediamine, tetrafluoro-para-phenylenediamine and 4,4'-diamino-octafluorobiphenyl. Of the three, the meta isomer
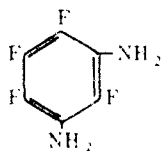
is most suitable for use as a curing agent for epoxy resins. This material is supplied as a gray powder with a purple tint and has a melting point of 130 C. The molten material sublimes readily and also reacts with oxygen in air to become deeply colored. However, it may be melted quickly and placed into liquid epoxy resins before loss or damage occurs.

Relative to the unfluorinated analogue, tetrafluoro-meta-phenylenediamine is a slow curing agent for epoxy resins. A typical epoxy resin is "B"-staged slowly at temperatures as high as 100 C. Between 100 and 160 C curing reactions proceed at reasonable rates, and strong plastics are produced. The fluorinated epoxy resins I and II (see previous sketches) were both converted to rather strong plastics, which apparently carried fluorine on all of the available ring positions.

Tetrafluoro-m-phenylenediamine has been used to advantage as a curing agent for 1,4-cyclohexane dioxide. This small-molecule diepoxide has been used to produce plastics with exceptionally high compressive strengths (2). However, it is difficult to use in a conventional fashion because of excessive volatility during the cure cycles, a potential for destructive reaction during cure, and poor performance of the plastic in water immersion. The use of fluorinated diamine allows the resin to be bodied under closed-vessel conditions (6) until a manageable composition is obtained. It can be retained in a partially reacted condition indefinitely and cured to plastic with an ultimate compressive strength of more than 70,000 psi. The fluorinated plastic is somewhat more resistant to water effects than the normal composition (Fig. 1), but it also absorbs water to an excessive extent (Fig. 2, curve A).

The 1,4-cyclohexane dioxide system illustrates a basic difficulty in the synthesis of high-strength resins for use in water. The strength of plastic made from it reflects a tight molecular network which contains a high concentration of polar groups, specifically hydroxyl and amino groups. These groups have a high affinity for water, which interferes with the secondary cohesive forces arising from their presence. Improved

water resistance results when the strength-essential bonding regions of the plastic are diluted. For this reason, the inert portion of the plastic molecular structure should be as hydrophobic as possible, and epoxy concentration in the resin should be in proportion to the strength requirement.

FLUORINATED DIHYDROXY CURING AGENTS

The diglycidyl ether of octafluorobiphenyl reacts with 4,4'-dihydroxy octafluorobiphenyl to form the acetone-soluble plastic
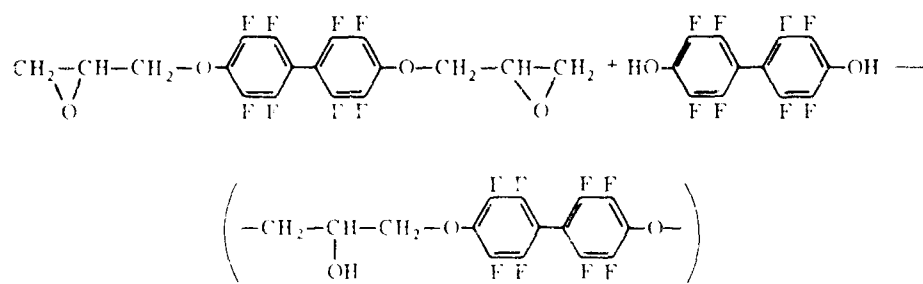
A stoichiometric amount of the purified components were melted and dissolved into one another at 100°C. After two hours, the temperature was raised to 120 C for 5 hr, and the reaction was completed at 165 C for 24 hr. The product was a light amber solid which formed clear brittle films from acetone.

In a similar manner, the fluoroepoxy reacted in a closed vessel with 2,2,3,3,4,4-hexafluoro-1,5-pentane diol during 24 hr at 165 C, and the product was the elastomeric polymer
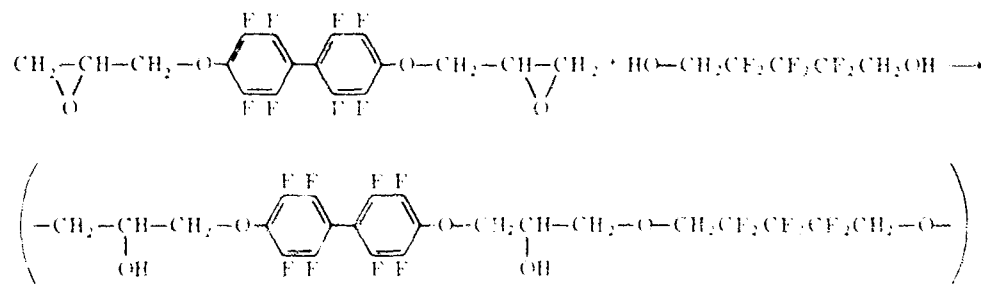
Fluorine on the diol apparently activates the hydroxyl group and makes it more aggressive toward the epoxy ring than a normal alcohol. The product may have some practical value for gaskets or seals.

PENDANT CHAIN EPOXY COMPONENTS

Advantage was taken of the reactivity of fluorinated alcohols with epoxy groups to attach pentadecafluorooctyl groups to a tetrafunctional epoxy resin. One half of the theoretically equivalent amount of fluoroalcohol was used. This allowed available epoxy

groups to remain unreacted for subsequent use in plastic formation. The following reaction represents an idealized picture of the synthesis:
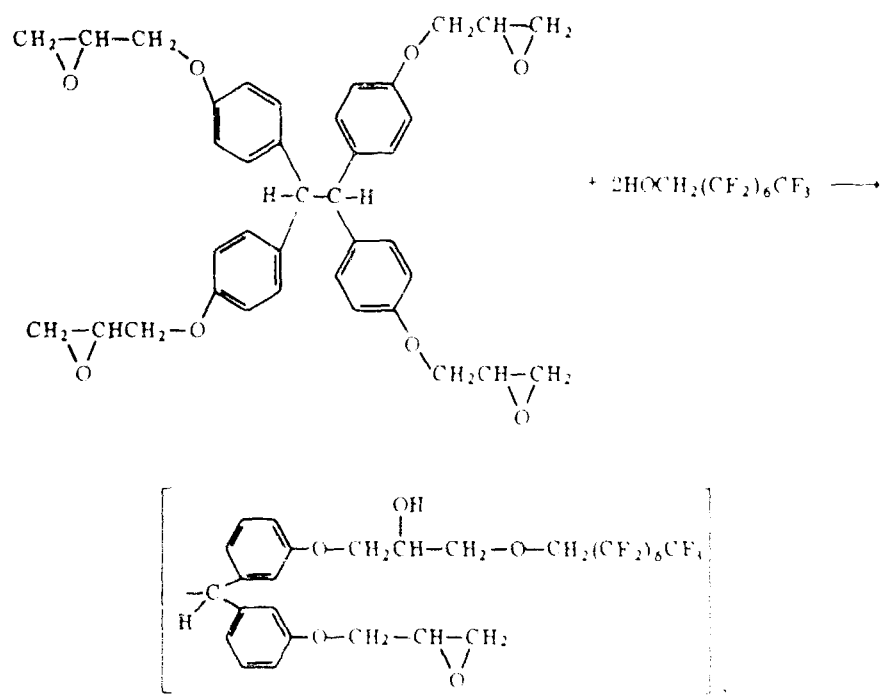
When blended with a Bisphenol-A resin and cured with an appropriate curing agent, this material shows promise as a water-insensitive filament-winding matrix.

The details of the above synthesis are: 1H,1H-pentadecafluorooctanol-1, 125.0 g, and Shell Chemical Company's Epon 1031 epoxy resin, 125.0 g, were placed into a single-necked, 500-ml, round-bottom flask equipped with a reflux condenser and a magnetic stirrer and heated to 160°C. The starting composition was an incompatible two-phase suspension of molten epoxy and fluoroalcohol. During 100 hr of reaction with vigorous stirring and alcohol reflux, the reactants became largely compatible. Fluoro-alcohol, 50.0 g, was stripped on a rotary evaporator to leave a 200-g residue of soft yellow wax. This wax was dissolved at 170 C in a 1:1 solution of Dow Chemical's D.E.R. 332 LC and Shell's Epon 828. The product was a somewhat incompatible softer wax having a fluorocarbon content of about 10% by weight.

Filament-wound NOL rings of fiberglass reinforcement were prepared from the material with the use of DuPont Chemical Company's MOCA (chlorinated methylene dianiline) in a 3:1 resin/curing-agent ratio. This composition was melted into a mandrel heated to approximately 100°C, and a single end of 204-filament glass was wound directly into the melt. The composite was then cured at 160°C for 72 hr. Such rings appear to have exceptional fatigue resistance under water; further evaluation of the system is in progress.

PENDANT CHAIN CURING AGENTS

Since the ester linkage between an organic acid and a fluorinated alcohol is exceptionally stable (7), the attachment of pendant chains of fluorocarbon to curing agents via esterification reactions is an attractive process. A suitable reaction is
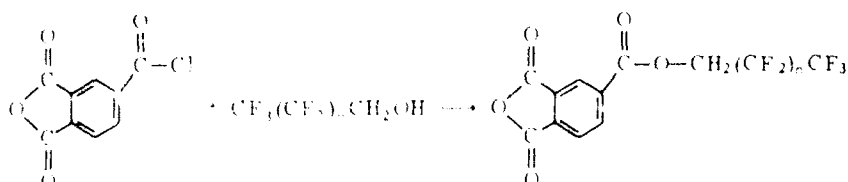
The greater reactivity of the acid chloride group in esterification allows the production of the anhydride ester without major loss of the anhydride function, which can be used subsequently to cure an epoxy resin. Alternately, a polyacid chloride can be partially esterified and the excess acid chloride groups hydrolyzed to make a polyacid curing agent with pendant fluoroester:
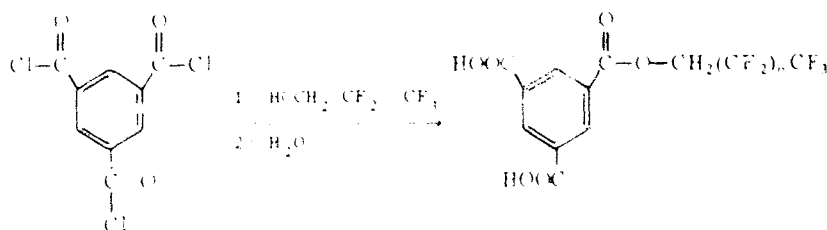
This procedure, however, is not as attractive in general as that above because polyesterification occurs, making isolation of the desired product difficult, and the physical characteristics of the diacids are not as favorable as those of anhydrides for use as epoxy curing agents.

THE MONOESTER OF TRIMESIC ACID AND 1H,1H-PENTADECAFLUOROOCTANOL-1

Equimolar quantities of trimesoylchloride and the fluoroalcohol were heated and stirred at 120°C for 4 hr while the disappearance of alcohol was followed by use of a gas chromatograph. The product was washed with warm water to hydrolyze excess acid chloride. The resulting white solid was soluble in acetone, except for a small amount of triester which was removed by filtration. Water was added to the acetone solution until all solids had precipitated. Most of this precipitate was then dissolved in methanol. The diester, which was insoluble, was removed by filtration. Dilution of the methanol solution with water gave a 35% yield of the desired monoester, which had sufficient purity for use as an epoxy curing agent. The elemental analysis and physical characteristics are:

$$C_{17}F_{15}H_9O_6$$
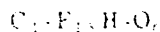
	Theory	Found
Carbon	34.57	34.97
Hydrogen	1.18	1.917
Fluorine	48.37	50.47
Neutral. equiv.	296	315

Melting point: 230 C

Major infrared bands: 1750, 1702, 1245, and 1210 cm^{-1}.

The material is somewhat difficult to use as a curing agent because of its high melting point and insolubility in epoxy resins at low temperatures. At high temperatures, it cures a Bisphenol-A epoxy readily, however, and the resulting plastic has slight affinity for water. (Water absorption curves will be presented in a later section.)

THE MONOESTER OF TRIMESIC ACID AND 1H,1H-HEPTAFLUOROBUTANOL-1

This monoester was prepared from trimesoyl chloride and the fluoroalcohol by reaction of equimolar amounts in toluene solvent for 4 hr under reflux with aluminum chloride catalyst. After solvent removal, the purification was essentially the same as that for the octyl ester, except for the change necessitated by the solubility of both the mono and diesters in methanol. The diester precipitated first when methanol was diluted with water. The elemental analysis and physical characteristics are:

$$C_{13}F_7H_7O_6$$

	Theory	Found
Carbon	39.8%	40.6%
Hydrogen	1.??%	2.93%
Fluorine	33.9%	34.0%

Melting point: 293°C
Major infrared bands: 1750, 1710, and 1235 cm^{-1}.

This ester melts at a higher temperature than the octyl derivative and also must be used at high temperatures to cure epoxies.

PENTADECAFLUOROOCTYL TRIMELLITATE ANHYDRIDE

This fluoroester anhydride was prepared by heating trimellitic anhydride acid chloride with the fluorooctyl alcohol at 120°C for 4 hr. It was purified by recrystallization from benzene and ligroin, and a yield of 50% was obtained. The elemental analysis and physical characteristics are:

$$C_{17}F_{15}H_5O_5$$

	Theory	Found
Carbon	35.6%	35.0%
Hydrogen	0.87%	1.93%
Fluorine	49.6%	50.2%

Melting point: 109°C
Major infrared bands: 1863, 1796, 1747, 1243, and 1212 cm^{-1}.

HEPTAFLUOROBUTYL TRIMELLITATE ANHYDRIDE

1H,1H-heptafluorobutanol-1 and trimellitic anhydride acid chloride were heated to 100°C for 24 hr. The product was obtained in 45% yield by recrystallization from the benzene-ligroin solution. Major characteristics are:

$$C_{13}F_7H_5O_5$$
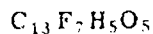
	Theory	Found
Carbon	41.7%	41.7%
Hydrogen	1.34%	2.71%
Fluorine	35.6%	36.1%

Melting point: 79°C
Major infrared bands: 1861, 1791, 1743, and
1234 cm^{-1}.

Because of the relatively low melting points, these anhydrides are easily dispersed into common epoxy resins. An initial incompatibility, when present, faded as the curing reactions progressed. The curing ability of the anhydrides was tested in small aluminum pianchets (1-in.-diam dishes). Compositions which were considered to be approximately stoichiometric were heated on a hot plate until compatible at about 200°C, and final cure was effected during 24 hr in an oven at 140°C. The planchets were covered during the cure to prevent excessive sublimation of the curing agents.

With a Bisphenol-A resin, the anhydrides reacted rather slowly to gel and produced fairly strong plastics after total cure. With the fluoroepoxies described previously, they produced weak plastics which were highly hydrophobic on the free-cast surfaces as evidenced by the ease with which water was shed as droplets.

INTERNAL ABSORPTION OF WATER

Small discs (1 in. diam x 1/8 in. thick) of the fluoroepoxies and curing agents were immersed in distilled water at ambient temperature. Periodically they were removed, quickly dried on the surface, and weighed to determine weight increases due to internally absorbed water. Figure 2 shows the water absorption behavior curves during 5 weeks of immersion for the following plastics:

Curve	Epoxy	Curing Agent
A	1,4-cyclohexane diepoxide	tetrafluoro-m-phenylenediamine
B	fluoro-resorcinol diglycidyl ether	tetrafluoro-m-phenylenediamine
C	liquid Bisphenol-A type	fluorobutyl ester of trimesic acid
D	4,4'-octafluorobiphenyl diglycidyl ether	tetrafluoro-m-phenylenediamine
E	liquid Bisphenol-A type	fluorobutyl ester of trimellitic anhydride
F	liquid Bisphenol-A type	fluorooctyl ester of trimesic acid
G	fluorooctyl tetrafunctional type	tetrafluoro-m-phenylenediamine
H	4,4'-octafluorobiphenyl diglycidyl ether	4,4'-dihydroxy octafluorobiphenyl
I	liquid Bisphenol-A type	fluorooctyl ester of trimellitic anhydride
J	liquid Bisphenol-A type	m-phenylenediamine

The data on Fig. 2 indicate several effects which will probably be observed generally as fluorocarbon is introduced into epoxy plastics: (a) Long perfluoroaliphatic chains are more effective than an equal concentration of short chains in making the plastics less water absorptive; (b) Aromatic fluorocarbon is not as effective as aliphatic, unless the fluorocarbon portion constitutes a high percentage of the total material; (c) Very-high strength plastics may be improved by the use of fluoroaromatic curing agents, but they remain exceptionally water absorptive; (d) Plastics made from fluoroaromatic amines continue to absorb water over long time spans, while those made from fluoro-aliphatic anhydrides and acids quickly reach a plateau and absorb slowly thereafter;
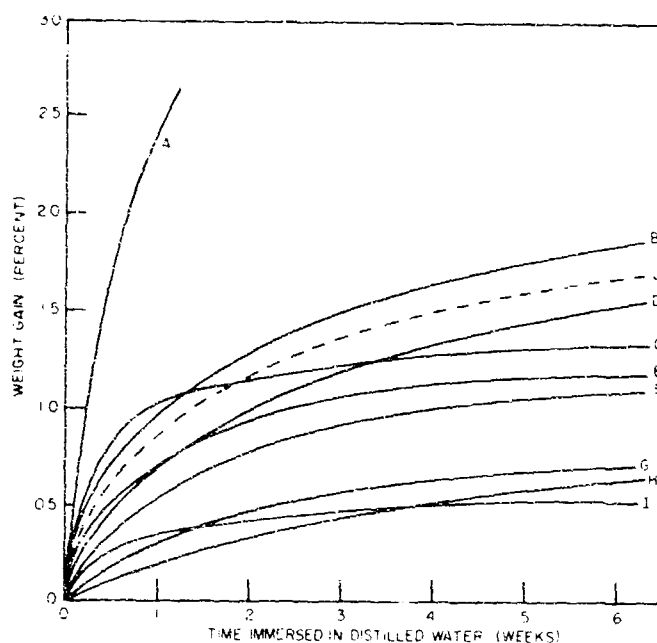
Fig. 2 – Water absorption characteristics of
fluoroepoxy plastics at 25°C over a 5-week
immersion period

(e) Water absorption is roughly inversely proportional to fluorine content and directly
proportional to polar group content; and (f) The effectiveness of water-absorption sup-
pression by fluorocarbon is dependent upon the types of polar groups present in the
cured plastic. For example, cured plastics with predominantly ester linkages are
suppressed more readily than those with a mixture of hydroxyl and amino groups.

SURFACE EFFECTS

The surface chemistry of these fluoroepoxy plastics has not been extensively ex-
plored because of the difficulty involved in obtaining representative surfaces. In most
cases, the removal of all traces of surface-active intermediates has proven difficult,
and a free-cast surface has different properties from one obtained by cutting and
polishing a cast sample. For example, a sample of resorcinol diglycidyl ether cured
with tetrafluoro-meta-phenylenediamine developed a free surface which had nearly the
same wetting properties as polytetrafluoroethylene. However, this surface was re-
moved easily by detergents and mechanical poli. ing to give a lower surface with essen-
tially the same wetting properties as a typical n nfluorinated epoxy.

The free-cast surfaces produced by epoxies containing long fluoroaliphatic chains
frequently have water contact angles greater than 90° (Fig. 3). Water is shed readily
from these surfaces, and they are usually durable. Practical use may be made of this
property to produce nonwetting coatings or to protect seams of joints which are bonded
with common adhesives. This could be particularly valuable as a protective layer for
adhesives which are exposed to water intermittently, such as bonded areas of aircraft
structures.

An epoxy plastic produced from Epon 1031 and 1H,1I pentadecafluorooctanol-1 was
cured with a common liquid anhydride, whi, h has the ability to scavenge the free

Fig. 3 - Water-shedding ability of a
la;. joint bonded with fluoroepoxy

fluoroalcohol residue. Friction measurements were made on a surface obtained by
cutting the plastic and polishing the exposed areas. The static coefficient of sliding
friction μ_s was 0.16, and the kinetic coefficient μ_k was 0.10. These values are practi-
cally the same as those of high-density polyethylene, and are lower than those of most
unfluorinated plastics (8). This material could be useful because of the convenience
with which a liquid resin can be molded to produce plastics with low surface friction.
Self-lubricating gears or sliding mechanisms on guns are some potential applications.

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13 ABSTRACT

Some epoxy plastic components (resins and curing agents) have been synthesized which contain fluorocarbons in their molecular structures. In some cases the fluorocarbon is part of the network structure upon which the strength of the plastic depends, and in all cases it is attached to the network by at least one covalent chemical bond. Among the properties that are obtained with selected resin systems are surface nonwetting by water, low internal absorption of water, and low surface friction of the cured plastics. In specific cases, low-melting or liquid resin systems have been obtained which react upon the application of heat to yield plastics.

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Fluorohydrocarbons						
Epoxy resins						
Plastics processing						
Wettability						
Mechanical properties						